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(54) Title: DEWATERING OF PEROXYGEN FORMULATIONS USING PERVAPORATION.

(57) Abstract: The invention relates to the removal of water from peroxygen formulations using pervaporation or vapor permeation. This method enables removal of water above the self-accelerating decomposition temperature of the peroxygen formulation. The formulations thus obtained have an improved stability. The invention also relates to the cleaning of contaminated membranes with a peroxygen formulation. Cleaning and water removal can be performed simultaneously.

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DEWATERING OF PEROXYGEN FORMULATIONS USING PERVAPORATION

- 5 The invention relates to a process of removing water from a peroxygen formulation.

Such a process is known from DE-A-28 55 860, in which soluble sulfates are added to organic peroxides in order to remove water by layer separation. This
10 process has the disadvantage that traces of salt remain in the organic peroxide, which reduces its stability considerably.

US 4,995,983 discloses a process where a peroxide waste stream is first freed of impurities in a first reverse osmosis or a nanofiltration step. Following the first step, the peroxide is first ionized by the addition of a base salt so as to increase
15 the pH of the stream, and subsequently the stream is subjected to a second reverse osmosis step in order to remove water from the stream. Reverse osmosis depends heavily on the pressure of the stream; the higher the pressure, the higher the flux. Pressures of up to 60 bars are not uncommon, which is undesirable as this brings about the use of equipment specifically
20 suitable for these high pressures. Another disadvantage is that traces of the base salt remain in the peroxide, which is detrimental to its stability and thus undesirable.

It is an object of the present invention to provide a process for removing water
25 from a peroxygen formulation resulting in a more concentrated peroxygen formulation having an improved stability.

We have found that if water is removed from the formulation using pervaporation, a formulation with an improved stability with respect to the salt-
30 containing formulations of the prior art can be obtained.

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Accordingly, the invention is a process of removing water from a peroxygen formulation comprising a pervaporation or vapor permeation step wherein the water is transported through a semipermeable membrane. The techniques of pervaporation and vapor permeation enable the selective removal of water from the formulation, as the transport of water through the semipermeable membrane is faster than the transport through it of the peroxygen. Hence, with the process of the invention water can be removed without the addition of a salt to the peroxygen formulation, resulting in a more concentrated peroxygen formulation with a higher stability. A higher stability further enables storage in larger quantities. The high stability furthermore enables water removal at a higher temperature relative to conventional processes which improves the water flux through the membrane resulting in a higher productivity of the applied pervaporation or vapor permeation device. Another advantage is that the process of the invention can be applied to a wider range of peroxides, thus also the peroxides which cannot be dewatered by addition of salt due to stability problems.

In WO 99/59711 a process is disclosed for the preparation of an organic compound, not a peroxygen, by a condensation process at a temperature above 80°C. In this process, water formed during the condensation is removed by pervaporation. This water removal serves to shift the condensation equilibrium to the condensate side, thus effectively enhancing the reaction rate. In the process of the present invention pervaporation is used to remove water from a peroxygen formulation, which is not disclosed in WO 99/59711.

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Membranes of the process of the invention are semipermeable membranes which are as such known to the skilled person. These membranes are able to separate molecules through a difference in diffusive flux of the molecules. Transport mechanisms of molecules through the membrane are commonly

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known and may depend on a difference in adsorption onto the membrane between the molecules, a difference in diffusivity of the molecules, or on a difference in size of the molecules to be separated (viz. via molecular exclusion), for example. Through these properties a semipermeable membrane is clearly distinguished from conventional permeable membranes having for example relatively large pores (with sizes in the order of microns or even larger). Suitable semipermeable membranes are polymer-based membranes, inorganic membranes, and mixed-matrix membranes, for example. The polymer-based membranes generally are dense membranes. Such dense membranes may comprise a polymer matrix with a thin dense top layer, whereby the hydrophilic (or hydrophobic) properties of the matrix and the top layer may be the same or differ. The hydrophilicity of the polymer applied in the dense membrane is an important parameter which determines the size of the water flux through the membrane and the selectivity towards water relative to more hydrophobic components. Examples of polymers suitable for use in such polymer-based membranes are polyvinyl alcohol which can be cross-linked, cellulose, cellulose acetate, chitosan, mixed polymers, grafted polymers, polysulfone, and polyacrylonitrile. The polymer matrix and/or the dense top layer can be made from one or more of the aforementioned polymer materials. Inorganic membranes generally are microporous membranes. Examples of such inorganic membranes are ceramic membranes comprising any type of zeolite, alumina, zirconia, titania, or amorphous materials such as silica, or a combination thereof. The inorganic membrane used in the process of the invention has a pore size of at least 0.2 nm, preferably at least 0.25 nm, and most preferably at least 0.3 nm, and at most 1.5 nm, preferably at most 1 nm, and most preferably at most 0.5 nm. The pore size distribution is an important parameter that determines the separation power of the membrane. If the membrane has a relatively large amount of larger pore sizes, larger molecules, i.e. molecules with a large kinetic diameter, can also pass the membrane and

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the separation power will be relatively low. If, in contrast, the membrane has a relatively large amount of smaller pore sizes, predominantly water will pass the membrane and the separation power will be high.

5 A mixed-matrix membrane is a membrane comprising a combination of an inorganic and an organic material, such as a ceramic membrane coated with a polymer layer, or a polymer matrix impregnated with an inorganic material.

The membrane of the invention can be of any suitable shape depending on the application in which it is used. It can have the shape of a flat plate, of a tube, of a hollow fibre, a monolith and of a wound spiral.

10

The peroxygen formulation of the invention can be any type of compound comprising a peroxygen group. Preferably, the peroxygen compound is a hydrogen peroxide or an organic peroxide, of which the hydrogen peroxide is less preferred. Examples of organic peroxides are diacyl peroxides, peresters
15 including percarbonates, peroxydicarbonates, perketals, ketone peroxides, dialkyl peroxides, hydroperoxides, peracids, or a combination of two or more organic peroxides.

The concentration of these peroxygen compounds in the formulation is at least 1 percent by weight (wt%), preferably at least 10 wt%, and most preferably at
20 least 25 wt%, and at most 99 wt%, preferably at most 90 wt% and most preferably at most 75 wt% of the total formulation.

A skilled person will understand that in the peroxygen formulation any conventional additive can be present in a desired amount. Such an additive may be for instance a non-ionic surfactant, a protective colloid, anti-freeze, pH-
25 adjusting agents, sequestering agents, and, if desired, biocides.

The process of the invention is carried out at any suitable temperature. Preferably, the temperature is at least 0°C, more preferably at least 10°C, and most preferably at least 20°C, and at most 200°C, preferably at most 150°C,
30 more preferably at most 100 °C, and most preferably at most 80°C.

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- On one side the semipermeable membrane is brought into contact with the peroxygen formulation. On the other side of the membrane (permeate side) the partial pressure of water is lower than the partial vapor pressure on the formulation side, so as to create a driving force for transport of water through the membrane. In case pervaporation is used, the partial vapor pressure is defined as the product of the mole fraction of water, the activity coefficient of water, and the saturated vapor pressure of water at the applied temperature. When vapor permeation is used, the partial pressure is defined as the product of the mole fraction of water in the vapor and the total vapor pressure.
- 5
- 10 Preferably, the pressure at the permeate side is chosen so low that the permeate (which is mainly water) is actively removed, i.e. the partial pressure of water on the permeate side is lower than the partial pressure of water on the formulation side. Such removal can be reached by evacuation, e.g. with a vacuum pump, or by flowing a gas along the membrane, e.g. an inert gas such
- 15 as N₂, He or Ar. Preferred absolute pressures at the permeate side are at least 1 mbar, preferably at least 2 mbar, and most preferably at least 5 mbar, and at most 1 bar, preferably at most 500 mbar, more preferably at most 100 mbar, even more preferably at most 75 mbar, and most preferably at most 50 mbar.
- 20 The peroxygen formulation can be dewatered with any conventional pervaporation or vapor permeation device. The formulation can be brought into contact with the membrane once. It is further contemplated to have a multitude of membranes set in series, so that the formulation will be in contact with all the membranes one after the other. It is also possible for the peroxygen
- 25 formulation, once it has passed the membrane, to be recirculated in a circulation pervaporation or vapor permeation apparatus, after which the formulation may again be brought into contact with the same membrane.
- The formulation from which water is at least partially removed after it has passed the membrane can be stored in a storage tank. The storage tank can

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be a tank separated from the pervaporation or vapor permeation apparatus or it may be part of the circulation pervaporation or vapor permeation apparatus.

Also devices suitable for pervaporation or vapor permeation are envisaged comprising one or more separation elements comprising a first hollow tube which is surrounded by a second hollow tube which is in turn surrounded by a cooling and/or heating element. The first hollow tube is at least partially made of a tube-shaped semipermeable membrane in which the permeate is actively removed, e.g. by a vacuum or a flowing gas. Between the first and the second tube the peroxide formulation may be flown either in liquid or gaseous form. An example of a device having a plurality of separation elements is the PERVAP® SMS ex Sulzer Chemtech. An advantage of such a device is that the volume of the formulation which is present in the device, is relatively small, therewith reducing the danger of explosion considerably. Moreover, the temperature within each separating element can be controlled actively and accurately, whereby the temperature of the peroxide present in the element is easily adjusted in a relatively short period of time, reducing the explosion risk even more. This configuration also enables a large contact area of the formulation with the semipermeable membrane. Consequently, the water removal rate is relatively high, and dewatering can be performed in a short period of time relative to conventional pervaporation or vapor permeation devices.

The process of the invention can be performed at any suitable temperature. In common pervaporation or vapor permeation devices the temperature chosen for dewatering is generally below the self-accelerating temperature (SADT) of the formulation in said device. In the process of the invention the dewatering temperature can also be chosen below the SADT of the formulation in the pervaporation or vapor permeation device. The SADT of a peroxygen formulation depends on the type of peroxygen and the (storage) volume of the

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formulation, for example, as can be learned from "Initiators for high polymers" from Akzo Nobel Chemicals bv.

However, the inventors have now found that, it is possible to dewater a peroxide formulation at a temperature at or above the SADT of the formulation in the device, while still securing safety. Preferably, dewatering at such high temperatures is performed in a device having one or a plurality of separation elements. At this relatively high temperature, the water flux through the membrane is improved even more resulting in an increased productivity of the pervaporation or vapor permeation device. Preferably, the temperature of the formulation in the process of the invention is at least 50 °C, preferably at least 60 °C, more preferably at least 70 °C, and most preferably at least 80 °C, and at most 200 °C, preferably at most 150 °C, more preferably at most 100 °C, and most preferably at most 90 °C. Preferably, the period of time during which the formulation is at a temperature at or above SADT, is shorter than the induction time of the formulation at that temperature. The heating and cooling of the formulation can be performed within the device itself or outside the device with a separate cooling and/or heating device.

The purity of the dewatered formulation is generally chosen such that formulation is stable. Preferably, the dewatered formulation comprises at least 10 wt%, preferably at least 20 wt%, more preferably at least 25 wt%, and most preferably at least 30 wt%, and at most 80 wt%, preferably at most 85 wt%, more preferably at most 90 wt%, and most preferably at most 99 wt%. The purity level of the peroxygen formulation that can be obtained depends on the stability of the dewatered formulation, which in turn depends on the type of peroxygen.

The permeated water that is obtained with the process of the invention has a relatively high level of purity. Purity levels of above 95 wt%, preferably above 98 wt%, and most preferably above 99 wt% of water in the permeate can be obtained.

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It is also envisaged to remove at least partially a first peroxygen together with water from a peroxygen formulation comprising a second peroxygen. The first and second peroxygen must differ so much that it is possible to separate them with the process of the invention; the first peroxygen may be smaller in size than the second, or the first may be more hydrophobic than the second peroxygen (or vice versa), for example. The first peroxygen can be any type of peroxygen, and is preferably hydrogen peroxide or an organic peroxide. Hydrogen peroxide is most preferred.

10

Hydrogen peroxide, hydroperoxide, and peracid formulations from which water is removed according to the process of the invention can be used to prepare an organic peroxide, such as an organic hydroperoxide. In other words, the dewatered formulation can be a raw material for the production of organic peroxides. The advantage of using dewatered formulations in this process is that the preparation of the organic peroxide is performed in a shorter time with a higher space-time yield as compared to conventional processes with water-containing formulations. For the process less of the formulation is required to obtain the same quantity of organic peroxide, which is also cost-saving.

15

These advantages are also apparent when the dewatered formulation is used in any other kind of conventional chemical process, such as a bleaching process or a polymerization reaction. A preferred example of such a process is the use of an organic hydroperoxide in peroxidation processes.

20

A further aspect of the invention is a process for cleaning a contaminated membrane with a peroxygen formulation using pervaporation and/or vapor permeation. The contaminated membrane can result from any process in which membranes according to the present invention can be used. In pervaporation or vapor permeation processes contaminants may adsorb or even react at the surface of the pore wall of the membrane, resulting in a lower separation power.

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It is therefore desirable to keep the membrane clean. The inventors have now surprisingly found that peroxygen compounds, e.g. hydrogen peroxide and organic peroxides, are suitable to remove contaminants from the membrane pore wall, in particular when the contaminant is of an organic nature.

- 5 Preferably, hydrogen peroxide which is generally diluted with water, is used for this purpose. It is also contemplated to have a small amount of, e.g., hydrogen peroxide present in the peroxygen formulation in order to increase the cleaning capability. Preferably, at most 10 wt%, more preferably at most 5 wt%, even more preferably at most 2 wt%, and most preferably at most 1 wt% of hydrogen
- 10 peroxide will be present in the formulation.

- It is further envisaged that water is removed simultaneously with the process of cleaning. In this way, the membrane can be kept clean during the removal of water. This has the advantage that the separation power of the membrane will remain unchanged during the dewatering process and can be used for a
- 15 plurality of batches. It further enhances the lifetime of the membrane.

The invention as described above is illustrated with the following Figure and Examples.

- Figure 1 Schematic representation of a circulation pervaporation
- 20 apparatus.

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Examples

In Examples 1-6 a 70 wt% tert-butyl hydroxy peroxide (TBHP) formulation, Trigonox[®] A-W70 ex Akzo Nobel N.V., is dewatered using pervaporation.

- 5 Pervaporation as conducted in the examples is performed in a circulation pervaporation apparatus which is illustrated in Figure 1. TBHP is added to a circulation vessel 1, from which the peroxide is pumped through Teflon[®] tubes by means of and via a pump 2 to a membrane module 3. The membrane module 3 is connected to a cold trap 4, which in turn is connected to a vacuum
10 pump 5, and a tube 7 which is connected to the circulation vessel 1. From the tube 7 the formulation can be tapped, if desired, via an outlet 6.

- The membrane module comprises a ceramic membrane (ex ECN, The Netherlands, code S9-5_Ti12-1) with an amorphous silica top layer with a thickness of about 150 nm coated on an alumina support layer. The main
15 average pore diameter of the membrane is between 0.3 and 0.5 nm. The membrane is tubular in shape with the silica layer situated on the outside of the tube. The outer diameter of the membrane is 14 mm and the length of the membrane is 391 mm. The membrane area is 172 cm². The TBHP formulation was pumped from the circulation vessel to the membrane module at a flow of
20 360 litres per hour at atmospheric pressure.

The permeate separated by the membrane module is collected using the cold trap 4, which is cooled by liquid nitrogen. The analysis of the permeate was performed by determination of the refractive index using a refractometer. The concentration in the feed was analyzed using a GLC.

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Example 1

In this example Trigonox[®] A-W70 was diluted in a glass circulation vessel to a
5 TBHP weight fraction of 60 wt% and a water content of 40 wt%. At this
concentration the mixture is a two-phase system consisting of an organic phase
with 70% TBHP and an aqueous phase with about 85% water. The total starting
weight of the mixture was 1.5 kilograms. The temperature of the solution was
kept at 25°C during the whole experiment. The pressure applied on the
10 permeate side was 2 mbar.

Table 1

Time Minutes	Weight % H ₂ O in feed	Gram Permeate	Weight % H ₂ O in permeate	Total Flux Gram/sqmtr/h
0	41.89			
56	37.99	13.90	98.37	865
112	34.78	15.38	95.37	958
165	33.54	15.03	99.79	989
225	33.03	16.72	99.46	972
285	32.63	16.68	99.68	970
345	31.96	15.18	98.35	883
410	31.32	18.72	99.50	1,005

The results of Table 1 show that the water content in the formulation is
15 decreased by about 10 wt% using the pervaporation technique at 25°C. The
permeate has a purity of more than 99%, indicating that water is selectively
removed from the formulation.

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Example 2

In Example 2 Trigonox[®] A-W70 was dewatered at 25 and 35°C. The average vacuum applied on the permeate side of the membrane was 11 mbar. The starting weight of the solutions was 1,327 grams.

Table 2

Time Minutes	Weight % H ₂ O in feed	Gram Permeate	Weight % H ₂ O in permeate	Total Flux Gram/sqmtr/h
0	30.1			
45	29.88	10.67	98.62	827
105	29.11	14.38	98.93	836
170	28.48	14.93	98.97	801
232	27.99	14.88	99.10	837
300	27.49	15.20	99.08	780
375	26.52	18.27	99.21	850
406*	25.97	7.15	98.65	805
440	25.33	7.69	98.99	789
475	24.31	11.22	99.11	1,118
536	23.37	22.77	99.16	1,302
591	22.30	21.64	99.20	1,373
675	20.43	29.91	99.18	1,242
740	18.50	23.86	99.22	1,281
800	16.57	19.65	99.18	1,142
874	14.70	24.57	99.17	1,158

* Experiment was stopped for a short time; temperature reduced to 15°C; experiment continued at 35°C; at t= 406 minutes the temperature was again 25°C; only at t= 475 minutes the temperature was 35°C.

The formulation was dewatered from 70 wt% TBHP to 73 wt% at 25°C and was further dewatered to 85 wt% TBHP at 35°C. The purity of the permeate is about 99 wt% of water, indicating that water is selectively removed from the formulation.

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Example 3

Trigonox[®] A-W70 was dewatered at 45°C in Example 3. The average vacuum applied on the permeate side of the membrane was 18 mbar. The starting weight of the solutions was 1,379 grams.

Table 3

Time Minutes	Weight % H ₂ O in feed	Gram Permeate	Weight % H ₂ O in permeate	Total Flux Gram/sqmtr/h
0	29.69			
35		18.08	97.48	1,802
65	28.00	20.19	99.35	2,348
125	26.49	36.65	99.37	2,131
185		38.20	99.42	2,221
255	22.26	40.14	99.37	2,000
315		36.33	99.39	2,112
365	17.75	26.96	99.32	1,881
430	14.69	34.55	99.31	1,854
485	12.75	22.77	99.19	1,444
520*	11.10	10.22	95.74	1,019
563	9.39	15.49	98.88	1,257

* Experiment was stopped and continued the next day; temperature reduced to 15°C; at t= 520 minutes the temperature was again 42.8°C; at t= 538 minutes the temperature was again 45°C.

The TBHP formulation was dewatered from 70.3 wt% TBHP to 90.6 wt%. Also in this example the permeate is relatively pure, as about 99 wt% is water.

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Example 4

In this example dewatering of Trigonox[®] A-W70 at 55°C is described. The average vacuum applied on the permeate side of the membrane was 25 mbar.

- 5 The starting weight of the solutions was 1,201 grams.

Table 4

Time Minutes	Weight % H ₂ O in feed	Gram Permeate	Weight % H ₂ O in permeate	Total Flux Gram/sqmtr/h
0	20.10			
45	28.15	45.13	99.15	3,350
90		39.49	99.27	3,204
124	23.40	33.80	99.35	3,187
180		45.86	99.24	3,018
225	15.93	38.05	99.28	2,950
270		30.41	99.15	2,357
325	9.77	32.49	99.12	2,061

- 10 The formulation was dewatered from 69.9 wt% TBHP to 90.2 wt%. Again water is selectively removed from the formulation.

Example 5

- 15 Example 5 describes an experiment wherein Trigonox[®] A-W70 was dewatered at 65°C. The average vacuum applied on the permeate side of the membrane was 30 mbar. The starting weight of the solutions was 1,424 grams.

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Table 5

Time Minutes	Weight % H ₂ O in feed	Gram Permeate	Weight % H ₂ O in permeate	Total Flux Gram/sqmtr/h
0	31.22			
25	28.69	30.33	98.86	4,232
52	27.09	32.45	99.49	4,193
77	25.61	28.43	99.53	3,967
113	22.93	41.27	99.56	3,999
142	21.43	32.53	99.56	3,913
177	19.41	32.46	99.52	3,235
207	17.24	27.33	99.50	3,178
237	15.51	23.72	99.48	2,758
285	13.46	36.99	99.49	2,688
334	11.04			
345	10.39	36.31	99.45	2,111

The TBHP was dewatered from 68.8 wt% TBHP to 89.6 wt%. The selectivity of the membrane for water appears to increase compared to the results of Examples 2-4. The purity of the permeate is now about 99.5 wt% of water.

Example 6

Dewatering of Trigonox[®] A-W70 at 75°C is monitored in Example 6. The average vacuum applied on the permeate side of the membrane was 35 mbar. The starting weight of the solutions was 1,358 grams.

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Table 6

Time Minutes	Weight % H ₂ O in feed	Gram Permeate	Weight % H ₂ O in permeate	Total Flux Gram/sqmtr/h
0	29.27			
10		15.46	98.21	5,393
33	27.66	39.00	99.57	5,915
63	24.61	45.84	99.60	5,330
77		21.63	99.61	5,390
124	19.34	60.53	99.56	4,493
170	15.65	53.37	99.54	4,047
210	12.70	37.11	99.46	3,236
235	10.93	21.19	99.43	2,957
267	9.56	21.31	99.35	2,323
290	8.59	14.35	99.32	2,176

The TBHP was dewatered from 70.7 wt% TBHP to 91.4 wt%. As in the case of the results of Example 5, the removal of water proceeds selectively, with the permeate containing about 99.5 wt% of water.

Example 7

In Example 7 the thermal stability of the formulations obtained in Examples 2-6 were determined using DSC-scans carried out in closed pyrex cups. The DSC was heated from 28 to 220°C at a rate of 2°C/min. The heat flow was recorded as a function of temperature. The temperature at which the heat flow is equal to 100 Watt/kg gives a good indication of the thermal stability of the sample. These results are given in Table 7 below.

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Table 7

Sample	Content (%)	Temp. at which Q = 100 W/kg (°C)
Starting material TBHP-70 ex.	70	119
Pervaporation exp. Example 2		
Sample 1 after pervap. at 25°C	73	121
Sample 2, after pervap. at 35°C	78	121
Sample 3, after pervap. at 35°C	85	116
Pervap. Exp. Example 3		
Sample 1, after pervap. At 45°C	85	115
Sample 2, after pervap. At 45°C	90.6	110
Pervap. Exp. Example 4		
Sample 1, after pervap. at 55°C	90.2	111
Pervap. Exp. Example 5		
Sample 1, after pervap. at 65°C	89.6	110.6
Pervap. Exp. Example 6		
Sample 1, after pervap. at 75°C	91.4	104.5

5 The decrease in stability by pervaporation was only around 10°C for most of the samples, while the concentration was increased from 70 to 90 wt%. This is much better than is reached for comparable samples prepared in a traditional process. Such a traditional process of concentrating a TBHP formulation is by the addition of CaCl₂. The thermal stabilities of the formulations dewatered with CaCl₂ and pervaporation were determined using DSC. The results are tabulated in Table 8.

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Table 8

Sample	Predicted SADT from a DSC scan (°C)	Real SADT (°C)
TBHP-70% or Tx AW-70	70	80
TBHP-92% dried with CaCl ₂	30	35
TBHP-90% ex. Pervaporation	60	65

The thermal stability of TBHP-90% prepared by pervaporation is only decreased by about 15°C compared to the original TBHP-70 (i.e. Trigonox[®] A-W70). Concentrating the peroxide by using CaCl₂ gives a reduction of 45°C. These results indicate that dewatering by using pervaporation gives a TBHP formulation with a considerably higher stability. This more stable formulation can hence be stored in larger quantities.

10 Example 8

Example 8 describes a process of cleaning an amorphous silica pervaporation membrane with hydrogen peroxide.

The membrane was first intentionally contaminated with an organic compound according to the following procedure. The amorphous silica coated ceramic membrane (ex Sulzer Chemtech) with an effective membrane area of 57 cm² was used for the dewatering of an ethanol/water mixture containing several ppm monochloroacetic acid. The mixture contained 12 wt% water on the total weight of the mixture. The measurement conditions were: 70°C feed temperature, 2 mbar permeate pressure, and a feed flow of 200 litres of mixture per hour. The water flux through the membrane decreased by a factor of two and the process selectivity increased by a factor of three.

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For comparison reasons, a standard characterization test was performed with a clean butanol/water mixture on a non-contaminated amorphous silica pervaporation membrane. The mixture contained 5 wt% water and the measurement conditions were: feed temperature 75°C, permeate pressure 3 mbar, and feed flow 200 litres of mixture per hour. The average water flux measured was 1,558 grams/(m².h) with an average process selectivity of 693.

Cleaning of the silica membrane was performed by flushing the membrane with a solution of 2 wt% hydrogen peroxide at 30°C for 4 hours.

Following this cleaning step, a standard characterization test was performed with a clean butanol/water mixture. The mixture contained 5 wt% water and the measurement conditions were: feed temperature 75°C, permeate pressure 4 mbar, and feed flow 200 litres of mixture per hour. The average water flux measured was 2,173 grams/(m².h) at 5 wt% water in the feed with an average process selectivity of 960.

These results indicate that the amorphous silica membrane can be cleaned, in which process the productivity of the membrane and its selectivity are restored.

It is noted that an effective cleaning of the membrane surface depends on the properties of the adsorbed components. The use of specific organic peroxides can improve the efficiency of cleaning. Additionally, the concentration of the peroxide, the cleaning temperature, or the flow conditions can influence the effectiveness of the cleaning. The example given is not optimized, and a person skilled in the art can easily assess the optimal cleaning conditions.

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Example 9

As opposed to the ceramic membrane as used in the previous examples, the membrane module comprises a polymer-based membrane (GFT® 1510 ex
5 GFT). In this example Trigonox® A-W70 was dewatered at 40 °C for 400 minutes (0 to 400 minutes in Table 9). After 400 minutes of dewatering 80 g of water was added to the formulation, and the dewatering temperature was set at 30 °C. The flow rate of the formulation was 96 l/h. The pressure applied on the permeate side was 16 mbar.

10

Table 9

Time Minutes	Weight % H ₂ O in feed	Gram Permeate	Weight % H ₂ O in permeate	Total Flux Gram/sqmtr/h
0	31.57			
15		20.52		4830
100	30.38	32.23	77.71	1340
167	29.85	19.51	94.76	1030
230	28.33	12.22	95.82	680
265	28.06	12.32	95.81	1240
308	36.98	16.07	97.46	1320
355	26.15	16.61	97.58	1250
400		19.16	98.20	1500
1345	17.88			

In Table 9 it is shown that the TBHP formulation can be dewatered at 40 °C and at 30 °C. The purity of the permeate is about 95 wt% of water and higher
15 indicating that water is selectively removed from the formulation.

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CLAIMS

1. Process of removing water at least partially from a peroxygen formulation comprising a pervaporation or vapor permeation step wherein the water is transported through a semipermeable membrane.
5
2. Process according to claim 1 wherein the semipermeable membrane is an inorganic membrane including a ceramic membrane.
- 10 3. Process according to any one of claims 1 and 2 wherein the semipermeable membrane is used having a pore size of between 0.2 and 1.5 nm, preferably 0.3-0.5 nm.
- 15 4. Process according to claim 1 wherein the semipermeable membrane is a polymer-based membrane.
5. Process according to any one of the preceding claims wherein water is removed at a temperature at or above the SADT of the peroxygen formulation.
20
6. Process according to any one of the preceding claims wherein the peroxygen is hydroperoxide or an organic peroxide.
- 25 7. Process according to any one of claims 1-5 wherein the peroxygen is a peracid.
8. Process to prepare an organic peroxide or a peracid with a peroxygen formulation from which water is removed at least partially according to any one of claims 1-6.
30

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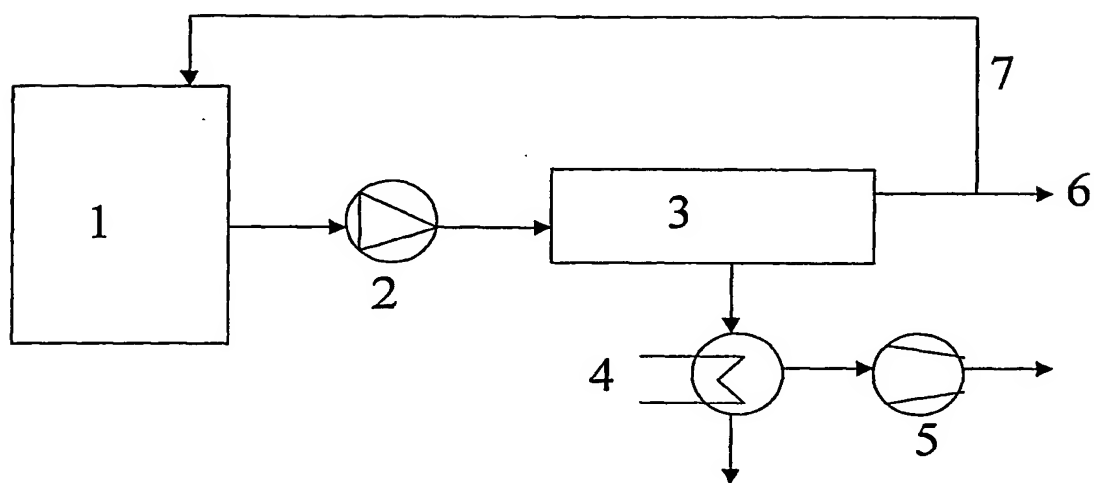
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9. Use of a dewatered peroxygen formulation obtainable from the process according to any one of claims 1-7 in a chemical process.
10. Use of a dewatered organic hydroperoxide formulation in a peroxidation
5 process.
11. Use of a peroxygen formulation for cleaning a contaminated semipermeable membrane in a pervaporation or vapor permeation process.
- 10 12. Use according to claim 11 wherein simultaneously water is removed from a peroxygen formulation according to any one of claims 1-7.

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Figure 1



INTERNATIONAL SEARCH REPORT

International Application No.

PCT/EP 03/11330

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07C407/00 C01B15/013 B01D61/36

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C C01B B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	IDEM	1
X	US 5 662 878 A (DATTA RATHIN ET AL) 2 September 1997 (1997-09-02) column 2, line 42 - line 67	11
A	IDEM column 4, line 17 - line 28 column 6, line 42 - column 7, line 27	1
A	US 5 488 177 A (APPEL HANS ET AL) 30 January 1996 (1996-01-30) claims	1
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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

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L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the International filing date but later than the priority date claimed

T later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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& document member of the same patent family

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 03/11330

C. (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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